

PATENT ABSTRACTS OF JAPAN

(11)Publication number :

2000-261008

(43)Date of publication of application : 22.09.2000

(51)Int.Cl.

H01L 31/04

(21)Application number : 11-063060

(71)Applicant : MITSUBISHI ELECTRIC CORP

(22)Date of filing : 10.03.1999

(72)Inventor : IMADA KATSUHIRO

MATSUNO YOSHINORI

HAMAMOTO SATORU

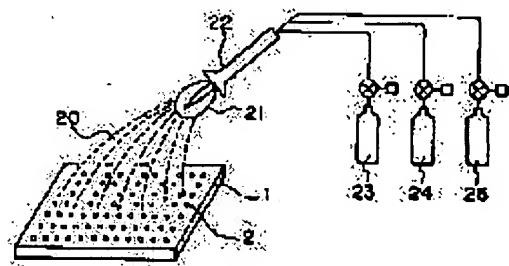
KAWAMA YOSHITATSU

(54) ROUGHENING METHOD OF SILICON SUBSTRATE SURFACE FOR SOLAR BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a roughening method of a silicon substrate surface for a solar battery, which improves the photoelectric conversion characteristic of the solar battery and can easily manufacture the battery at a low cost, and a polycrystalline silicon substrate manufactured by the method.

SOLUTION: The surface of a silicon substrate for a solar battery is roughened by a process which disperses and attaches fine particles 2 for a mask on the whole surface of a polycrystalline silicon substrate 1, a process etching a region of the substrate 1 surface on which region the fine particles 2 do not attach, and a process which eliminates the fine particles 2 left on the substrate 1 surface. The fine particles 2 for a mask are dispersed and attached on the whole surface of the polycrystalline silicon substrate 1, and the surface is etched. Thereby the region of the substrate surface, on which region the fine particles 2 do not attach, is preferentially etched. When the fine particles left on the mask are eliminated, the parts on which the fine particles 2 have attached become protrusions, and the parts on which the particles have not attacked become recesses. Uniform unevenness is formed on the surface, so that a polycrystalline silicon substrate having low reflection factor can be produced.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

JPO and INPI are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The surface-roughening approach of the silicon substrate for solar batteries which is the surface-roughening approach of the silicon substrate for solar batteries which endows detailed irregularity with the front face of a polycrystal silicon substrate, and includes the process which makes the particle for masks distribute and adhere to the front face of a polycrystal silicon substrate on the whole surface, the process which etches the field where the particle for masks on the above-mentioned front face of a substrate has not adhered, and the process which removes the particle for masks which remains from the above-mentioned substrate front face.

[Claim 2] The surface roughening approach of the silicon substrate for solar batteries according to claim 1 of the above-mentioned particle for masks mainly consisting of silicon oxide, and making the particle of the silicon oxide which supplies a gas-like silicon content compound into an oxyhydrogen flame, is made hydrolyzing, and is generated depositing on a polycrystal silicon substrate surface in the above-mentioned process which carries out adhesion.

[Claim 3] The surface roughening approach of the silicon substrate for solar batteries according to claim 1 of a polycrystal silicon substrate and a counter electrode being immersed in the solution which distributed the particle for masks, impressing predetermined direct current voltage to it, and making it electrodepositing the particle for masks on the front face of the above-mentioned substrate in the above-mentioned process which carries out adhesion.

[Claim 4] The surface roughening approach of the silicon substrate for solar batteries according to claim 1 to which screen-stencil the solution containing the particle for masks to a polycrystal silicon substrate surface in the above-mentioned process which carries out adhesion, and the particle for masks is made to adhere.

[Claim 5] The surface roughening approach of the silicon substrate for solar batteries according to claim 1 to which spray and spray the solution containing the particle for masks on a polycrystal silicon substrate surface in the above-mentioned process which carries out adhesion, and the particle for masks is made to adhere.

[Claim 6] The surface roughening approach of the silicon substrate for solar batteries according to claim 1 to which it is immersed, pull up a polycrystal silicon substrate in the solution containing the particle for masks in the above-mentioned process which carries out adhesion, and the particle for masks is made to adhere.

[Claim 7] The surface roughening approach of the silicon substrate for solar batteries any one publication of claim 1-6 which is made to rock a polycrystal silicon substrate and carries out dry etching in the above-mentioned process which carries out etching.

[Claim 8] The polycrystal silicon substrate for solar batteries whose reflection factor [in / the particle for masks is made to distribute and adhere to the whole surface, and it has the front face of the shape of detailed toothed which removed the particle for masks and was formed after dry etching, and / the wavelength of 628nm] is 25% or less.

[Claim 9] The surface roughening approach of the silicon substrate for solar batteries which sticks the screen for masks which is the surface roughening approach of the silicon substrate for solar batteries which endows detailed irregularity with the front face of a polycrystal silicon substrate, and has two or more detailed openings on a polycrystal silicon substrate to the whole surface, arranges it, and carries out dry etching through this screen.

[Claim 10] The surface roughening approach of the silicon substrate for solar batteries according to claim 9 which is made to rock a polycrystal silicon substrate and carries out dry etching.

[Claim 11] The polycrystal silicon substrate for solar batteries whose reflection factor [in / the screen for masks which has two or more detailed openings is stuck to the whole surface, and is arranged, and it has the front face of the shape

of detailed toothing formed by carrying out dry etching through this screen, and / the wavelength of 628nm] is 25% or less.

[Claim 12] The surface roughening approach of the silicon substrate for solar batteries which is the surface roughening approach of the silicon substrate for solar batteries which endows detailed irregularity with the front face of a polycrystal silicon substrate, cuts a polycrystal silicon substrate rough by machining, and carries out dry etching.

[Claim 13] The polycrystal silicon substrate for solar batteries whose reflection factor [in / it has the front face of the shape of detailed toothing formed by machining cutting a polycrystal silicon substrate rough and carrying out dry etching, and / the wavelength of 628nm] is 25% or less.

[Translation done.]

* NOTICES *

JPO and INPI are not responsible for any
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polycrystal silicon substrate for solar batteries obtained by the surface roughening approach of the polycrystal silicon substrate for solar batteries which is excellent in a low reflection factor at light absorption nature, and its approach in more detail about the surface roughening approach of the silicon substrate for solar batteries.

[0002]

[Description of the Prior Art] It is indispensable to high-performance-izing to incorporate light efficiently with photo-electric-conversion equipments, such as a solar battery. The approach of forming an antireflection film in a front face as the approach and the approach of endowing detailed irregularity with a front face are used. In the former, the light absorbed by the cross protection of the light in a film interface is amplified, and by the time the light which carried out incidence compared with the flat front face reflects, in order to carry out multiple-times reflection with irregularity, much light will be absorbed at the latter.

[0003] Generally in the solar battery using single crystal silicon, the processing which melts the front face of a silicon substrate in the alkali water solution of the sodium hydroxide of suitable concentration and temperature or a potassium hydroxide is used for a front face as an approach of granting detailed irregularity. Since the dissolution rate to an alkali water solution changes with crystal orientation, the field where a dissolution rate is slow exposes single crystal silicon to a front face. When a silicon (100) substrate is used, the field where a dissolution rate is slow (111) is exposed, and the irregularity on an about [number -100micrometer] detailed pyramid is formed. This structure is usually called texture structure.

[0004] However, by the polycrystal silicon substrate, since crystallographic-axis bearing has not gathered, since partial texture structure is unproducible, a reflection factor cannot be reduced by the technique by the above wet etching. For example, the reflection factor in the wavelength of 628nm is about 27 - 30% in the case where wet etching of the polycrystal silicon substrate is carried out to being about 15%, when a front face carries out wet etching of the silicon single crystal substrate of a field (100) about 36% with the silicon by which mirror polishing was carried out.

[0005] Then, it changes into the conventional wet etching and the approach of forming irregularity in the front face of a polycrystal silicon substrate at homogeneity is examined using approaches, such as machining, photolithography, and reactive ion etching. For example, Technical Digest of the International A V character mold groove is mechanically formed in PVSEC-9(1996) p.99, irregularity is formed, and the example which produced the solar battery is reported (drawing 10). Here, for 101, as for a table and 103, a substrate and 102 are [a blade and 104] cooling water. The V character mold groove with a depth of 70 micrometers is formed by making an edge press and **** the blade 103 of a V character mold on substrate 101 front face. And it is etching using the acid for removal of the damage layer by machining.

[0006] Moreover, Technical Digest of the International The example which formed the depression of 35-micrometer size by the approach of etching silicon in a sodium-hydroxide water solution PVSEC-7(1993) p.99 by using as a mask the silicon nitride which carried out pattern processing with photolithography is reported.

[0007] Moreover, Technical Digest of the International The example which formed detailed irregularity by reactive ion etching (it abbreviates to RIE hereafter) is reported to PVSEC-9(1996) p.109.

[Problem(s) to be Solved by the Invention]

[0008] However, when based on machining, since it tends to wear the blade of a V character mold out, frequent exchange is needed and it has the problem that a manufacturing cost becomes high. Moreover, when using photolithography, a process becomes complicated and a manufacturing cost is raised. Moreover, if RIE is used, while the substrate of a low reflection factor will be obtained, there is a problem that control of the reaction condition is difficult and mass production is not easy. Since it is easy to generate needlelike black silicon on a substrate front face when RIE is furthermore used, it is easy to damage a joint with N+ diffusion layer formed on it, and there is also a problem that the photoelectric transfer characteristic of a solar battery falls.

[0009] It was made in order that this invention might solve the above-mentioned trouble, and it aims at offering the polycrystal silicon substrate manufactured by the surface roughening approach of the silicon substrate for solar batteries with easily cheap manufacture which raises the photoelectric transfer characteristic of a solar battery, and its approach.

[0010]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, invention according to claim 1 The process which it is [process] the surface roughening approach of the silicon substrate for solar batteries which endows detailed irregularity with the front face of a polycrystal silicon substrate, and makes the particle for masks distribute and adhere to the front face of a polycrystal silicon substrate on the whole surface, It is the surface roughening approach of the silicon substrate for solar batteries including the process which etches the field where the particle for masks on the above-mentioned front face of a substrate has not adhered, and the process which removes the particle for masks which remains from the above-mentioned substrate front face.

[0011] The field where the particle for masks on the front face of a substrate has not adhered is preferentially etched by distributing all over a polycrystal silicon substrate, making the particle for masks adhere, and etching. Therefore, if the particle for residual masks is removed, the part to which the particle for masks had adhered serves as heights, the part which has not adhered serves as a crevice, uniform irregularity is endowed with a front face, and the polycrystal silicon substrate of a low reflection factor can be produced. Moreover, it becomes a flat configuration, N+ diffusion layer of sufficient reinforcement is formed, and the heights to which the particle for masks had adhered can raise the photoelectric transfer characteristic of a solar battery. Moreover, the cheaper surface roughening approach can be offered from facing making the particle for masks adhere, and not needing a complicated process like photolithography, and not needing machining.

[0012] Non-oxide ceramics particles which consist of resin for resists of acrylic or a synthetic-rubber system, such as oxide-ceramics particles, such as a particle, silicon oxide, and an alumina, SiC, and BN, can be used for the particle for masks used for the above-mentioned surface roughening approach that what is necessary is just what consists of matter which is hard to be etched from silicon. Moreover, the magnitude of the particle for masks has 0.5 micrometers - desirable 30 micrometers. If it is this range, since detailed irregularity can be formed and the concavo-convex height more than the wavelength of light will be obtained further, a reflection factor can be reduced further.

[0013] Moreover, invention according to claim 2 is characterized by making silicon oxide adhere to a substrate front face by the following approaches using the particle which mainly consists of silicon oxide as the above-mentioned particle for masks. That is, supply a gas-like silicon content compound into an oxyhydrogen flame, it is made to hydrolyze, and the particle of the silicon oxide to generate is made to deposit on a polycrystal silicon substrate surface. Since an affix is a hot silicon oxide particle, high adhesion force is obtained to a substrate and a silicon oxide particle does not exfoliate from a substrate front face in the early stages of etching. Moreover, since the silicon oxide obtained is a high grade, mixing of the impurity to a substrate can be controlled at the time of a surface roughening process.

[0014] Moreover, invention according to claim 3 is characterized by using the approach of a polycrystal silicon substrate and a counter electrode being immersed in the solution which distributed the particle for masks, impressing predetermined direct current voltage to it, and making it electrodepositing the particle for masks on the front face of the above-mentioned substrate in the above-mentioned process which carries out adhesion. Electrophoresis can be carried out and a substrate front face can be made to electrodeposit the particle for masks in homogeneity for a short time by setting up the polarity of a polycrystal silicon substrate so that it may have a particle for masks, and an opposite charge using the particle for masks which has the charge of plus or minus in the electrolytic solution, and impressing direct

current voltage.

[0015] Moreover, in the above-mentioned process which carries out adhesion, invention according to claim 4 screen-stencils the solution containing the particle for masks to a polycrystal silicon substrate surface, and is characterized by making the particle for masks adhere by removing a solvent. A substrate front face can be made regularly dotted with the particle for masks to which magnitude was more equal, and it can be made to adhere to it by passing opening of the above-mentioned screen.

[0016] Moreover, invention according to claim 5 is characterized by making the particle for masks adhere in the above-mentioned process which carries out adhesion by spraying the solution containing the particle for masks on a polycrystal silicon substrate surface, and removing a solvent. It can be made to adhere by generating the drop of uniform magnitude using easy equipment in the condition of having made the substrate front face distributing the particle for masks for a short time.

[0017] Moreover, invention according to claim 6 is characterized by being immersed, pulling up a polycrystal silicon substrate in the solution containing the particle for masks, removing a solvent, and making the particle for masks adhere in the above-mentioned process which carries out adhesion. It can be made to adhere, where the particle for masks is distributed by easy actuation for a short time.

[0018] Moreover, invention according to claim 7 is characterized by making a substrate rock and carrying out dry etching in the process which etches the polycrystal silicon substrate to which the particle for masks was made to adhere.

[0019] Invention according to claim 8 makes the particle for masks distribute and adhere to the whole surface, it has the front face of the shape of detailed toothing which removed the particle for masks and was formed after dry etching, and the reflection factor in the wavelength of 628nm is 25% or less of polycrystal silicon substrate for solar batteries.

[0020] Invention according to claim 9 is the surface roughening approach of the silicon substrate for solar batteries which endows detailed irregularity with the front face of a polycrystal silicon substrate, and is the surface roughening approach of the silicon substrate for solar batteries which sticks the screen for masks which has two or more detailed openings on a polycrystal silicon substrate to the whole surface, arranges it, and carries out dry etching through the screen.

[0021] Moreover, invention according to claim 10 is characterized by making a polycrystal silicon substrate rock and carrying out dry etching in invention of claim 9.

[0022] Invention according to claim 11 sticks the screen which has two or more detailed openings to the whole surface, and arranges it, it has the front face of the shape of detailed toothing formed by carrying out dry etching through this screen, and the reflection factor in the wavelength of 628nm is the polycrystal silicon substrate for solar batteries which is 25% or less.

[0023] Invention according to claim 12 is the surface roughening approach of the silicon substrate for solar batteries which endows detailed irregularity with the front face of a polycrystal silicon substrate, and is the surface roughening approach of the silicon substrate for solar batteries which cuts and carries out dry etching rough by machining about a polycrystal silicon substrate.

[0024] About a polycrystal silicon substrate, by machining, rough, it has the front face of the shape of detailed toothing formed by cutting and carrying out dry etching, and invention according to claim 13 is a polycrystal silicon substrate for solar batteries whose reflection factor in the wavelength of 628nm is 25% or less.

[0025]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing.

Gestalt 1. drawing 1 of operation is the mimetic diagram showing the adhesion process of the particle for masks concerning the gestalt 1 of this operation. Oxygen 23 and hydrogen 24 are supplied to a burner 22, an oxyhydrogen flame 21 is generated and the gas-like silicon content compound 25 is supplied into an oxyhydrogen flame 21 by making argon gas into carrier gas. Then, it hydrolyzes and the silicon oxide particle 20 generates a silicon content compound. The generated silicon oxide particle 20 is deposited on a substrate 1, and turns into the particle 2 for masks. And predetermined time etching is carried out according to the thickness of the silicon oxide particle 20 which deposited the substrate 1, and irregularity is endowed with the front face of a substrate 1. Next, the polycrystal silicon

substrate which carried out surface roughening is obtained by removing the particle 2 for masks which remains by etching.

[0026] As a silicon content compound used as the raw material of silicon oxide, silicon alkoxides, such as SiCl₄ or a tetra-ethoxy silane, can be used. By changing the speed of supply of a raw material etc., a silicon oxide particle with a particle size of 0.1 to 10 micrometers is producible.

[0027] Moreover, any of wet etching and dry etching may be used for etching. It is desirable to use for wet etching the mixed acid which mixed fluoric acid, a nitric acid, and water, or a sodium-hydroxide water solution. Again. It is desirable to use for dry etching RIE which uses fluorine gas or chlorine gas.

[0028] In addition, if the above-mentioned dry etching is performed rocking a substrate 1, the effectiveness of reducing the reflection factor of a substrate more will be acquired. Drawing 2 is the mimetic diagram showing the etching process in that case. 6 is a dry etching system and the substrate 1 to which the particle 2 for masks adhered is installed on the RF electrode 7 which has the stopper 8 which specifies the inclination and location of a substrate. The RF electrode 7 is connected to RF generator 11. 14 is reactant gas for etching and etching gas is emitted toward a substrate 1 from the ground electrode 9 which serves as a nozzle. Gaseous helium 13 is intermittently sprayed on the rear face to which the particle 2 for masks of a substrate 1 has not adhered, and it etches by making it rock so that it may incline for a while to the RF electrode 7. It is made for gaseous helium 13 to blow off from the hole established in several places other than the core of the RF electrode 7, and it changes the jet hole 10 frequently by the bulb 12. It is desirable to make it rock here so that the include angle of the RF electrode 7 and a substrate 1 may turn into 20 or less degrees.

[0029] When a substrate is not rocked to drawing 3 and it rocks with (a), the type section Fig. of the substrate of (b) is shown. When the side face of the part etched when not rocking rocked to perpendicularly near one, as for the side face, it had the taper of the include angle of 70 - 80 degrees. Since the area of the base of the etched part decreased when it rocked, it is thought that the reflection factor decreased.

[0030] Moreover, whether it rocks an electrode stage mechanically in addition to the approach of spraying gas from the above-mentioned substrate tooth back or uses the approach of rocking the nozzle which introduces reactant gas, the same effectiveness as the above is acquired.

[0031] The wet etching which uses fluoric acid may remove the silicon oxide particle to which the above remained, or it may be removed using the wet etching or dry etching using an above-mentioned mixed acid or an above-mentioned sodium-hydroxide water solution.

[0032] Particle size can make homogeneity and a small silicon oxide particle able to generate, and the silicon oxide particle of the elevated-temperature condition immediately after generation can be made to adhere to a substrate front face with the gestalt 1 of this operation by making the silicon content compound supplied by the shape of a gas hydrolyze in an oxyhydrogen flame. Therefore, the magnitude of the particle for masks becomes uniform, and since the adhesion force to a substrate is still larger, the effectiveness of not exfoliating easily at the time of etching is acquired. Therefore, uniform and detailed irregularity can be endowed with a substrate front face.

[0033] Gestalt 2. drawing 4 of operation is the mimetic diagram showing the adhesion process of the particle for masks concerning the gestalt 2 of this operation. It is immersed in the electrolytic solution 16 which distributed the particle for masks so that it may counter through predetermined spacing, and the substrate 1 and the counter electrode 17 are connected to DC power supply 19. And 18 is a cell. Here, let substrates 1 be a negative electrode and a positive electrode according to whether the particle for masks in a solution has the charge of plus or minus, respectively. And the particle for masks is made to electrodeposit on a substrate 1 by electrophoresis by carrying out predetermined time impression of the predetermined direct current voltage. Using the same approach as the gestalt 1 of operation, the substrate 1 which made the particle for masks electrodeposit removes the particle for masks which etches and remains, and obtains the polycrystal silicon substrate which carried out surface roughening.

[0034] The particle which consists of oxide ceramics, such as silicon oxide and an alumina, is [that what is necessary is just what has a charge in a solution as a particle for masks used for the gestalt 2 of this operation] desirable. Moreover, it is desirable to use for the electrolytic solution what added aqueous ammonia or organic ammonium salt as an electrolyte to the lower alcohol independent of a carbon number 1 - 4 ** or a mixed solvent with acetic ester.

[0035] Moreover, heat-treating is [after electrodepositing the particle for masks] desirable in order to heighten the adhesion force of solvent removal and a substrate, and the particle for masks. Whenever [stoving temperature] has 80

degrees C - desirable 150 degrees C.

[0036] According to the gestalt 2 of this operation, since the particle comrade for masks has a charge of the same kind in a solution, it exists in the condition of condensation having been controlled by the electric repulsive force and having distributed. Therefore, even if electrodeposited in a substrate, a distributed condition is maintained, and uniform irregularity is formed in a substrate front face of etching.

[0037] Gestalt 3. drawing 5 of operation is the mimetic diagram showing the adhesion process of the particle for masks concerning the gestalt 3 of this operation. It is made to stick all over substrate 1 front face, a screen 5 is arranged, and the solution 3 containing the particle for masks is screen-stenciled on it (a). And a screen 5 is removed, it is dotted with the particle 2 for masks at intervals of predetermined, and it obtains the substrate 1 by which patterning was carried out (b). The particle for masks which etches and remains using the same approach as the gestalt 1 of operation of this substrate is removed, and the polycrystal silicon substrate which carried out surface roughening is obtained.

[0038] The above-mentioned screen has [that what is necessary is just what cannot be easily etched by RIE which used fluorine gas etc.] a desirable screen made of the product made from stainless steel, or a fluororesin. Moreover, the magnitude of opening of a screen has 1 to desirable 50 micrometers.

[0039] Moreover, what cellosolve system solvents, such as ketone solvent, such as acetic ester, such as lower alcohol, such as a methanol, ethanol, and isopropyl alcohol, ethyl acetate, and butyl acetate, an acetone, and MEK, methyl cellosolve, and ethylcellosolve, a xylene, etc. were dissolved or distributed, and prepared the particle for masks can be used for the solution containing the particle for masks.

[0040] Since the particle pattern for masks with which keeps predetermined spacing and it is dotted by screen-stenciling the solution containing the particle for masks on a substrate is easily producible according to the gestalt 3 of this operation, uniform irregularity is formed in a substrate front face of etching.

[0041] Gestalt 4. drawing 6 of operation is the mimetic diagram showing the adhesion process of the particle for masks concerning the gestalt 4 of this operation. The solution 3 containing the particle for masks is sprayed on substrate 1 front face with an atomiser 4, and is sprayed, a solvent is removed, and the particle 2 for masks is made to adhere. When resin is used for the particle for masks, since the relation of drawing 7 between the coating weight of resin and a reflection factor is, it is important not to make resin adhere too much. Next, the particle for masks which etches and remains using the same approach as the gestalt 1 of operation of this substrate is removed, and the polycrystal silicon substrate which carried out surface roughening is obtained. In addition, on the same conditions as the gestalt 2 of operation, a substrate may be heat-treated, after making the particle for masks adhere. Moreover, a solution can use what was prepared like the gestalt 3 of operation.

[0042] Since a substrate front face can be made to distribute the particle for masks easily by spraying the solution containing the particle for masks on a substrate front face in the state of a minute drop according to the gestalt 4 of this operation, uniform irregularity can be formed in a substrate front face by continuing etching.

[0043] Predetermined time immersion of the gestalt 5. polycrystal silicon substrate of operation is carried out at the solution containing the particle for masks, except pulling up from a solution, the particle for masks which etches and remains using the same approach as the gestalt 1 of operation is removed, and the polycrystal silicon substrate which carried out surface roughening is obtained. Even if what the particle for masks dissolved is used for a solution, what carried out suspension distribution may be used for it. When using what carried out suspension distribution, after putting a substrate on the bottom of a container, putting a suspension solution into the container, making the particle for masks sediment and making it deposit on a substrate, pulling up from a solution is desirable. Moreover, a solution can use what was prepared like the gestalt 3 of operation.

[0044] According to the gestalt 5 of this operation, since a substrate front face can be made to distribute the particle for masks easily, uniform irregularity can be formed in a substrate front face by continuing etching.

[0045] Gestalt 6. drawing 8 of operation is the mimetic diagram showing the surface roughening approach concerning the gestalt 6 of this operation. The dry etching system of 6 is an RIE system, a substrate 1 is installed on the RF electrode 7 connected to RF generator 11, it sticks all over a substrate 1, and the screen 15 for masks is arranged. 14 is reactant gas for etching of CxFy gas, fluorine gas, or chlorine gas. Etching gas is emitted from the ground electrode 9 which serves as a nozzle, and etches the front face of a substrate 1 through the screen 15 for masks. The same screen can be used for the above-mentioned screen 15 for masks with having used for the gestalt 3 of operation.

[0046] Uniform irregularity is not only obtained, but according to the gestalt 6 of this operation, reinforcement with sufficient N+ diffusion layer formed on it is obtained by arranging the screen for masks and performing RIE on a substrate. This is considered because generating of needlelike black silicon is controlled compared with the case where he has no screen for masks.

[0047] Gestalt 7. drawing 9 of operation is the mimetic diagram showing the surface roughening approach concerning the gestalt 7 of this operation. Etching by RIE is performed by the same approach as the gestalt 6 of operation except having installed the substrate 1 rough-cut by machining on the RF electrode 7.

[0048] Although the concavo-convex height of the configuration of a crevice or heights of the substrate rough-cut by machining is uneven at an indeterminate form, irregularity is comparatively distributed over homogeneity and shows a comparatively low reflection factor. However, in order to remove the damage at the time of cutting, it was etching in the sodium-hydroxide water solution conventionally, as a result, the substrate front face became smooth, and the reflection factor was high. Since the damage at the time of cutting can be removed without making the reflection factor of the rough-cut substrate high according to the gestalt 7 of this operation, the photoelectric transfer characteristic of a solar battery can be improved. While irregularity employs efficiently the property of the rough cutting substrate comparatively distributed over homogeneity by etching the rough-cut substrate by RIE, the configuration of concave heights can be equalized and it thinks because irregularity can be further made detailed.

[0049] Hereafter, this invention is explained to a detail using an example.

[Example] SiCl₄ is supplied to an oxyhydrogen-flame burner by making argon gas into carrier gas, using SiCl₄ as an example 1. silicon oxide raw material, it hydrolyzes in a flame and a powder-like silicon oxide particle is produced, and the polycrystal silicon substrate (100mm angle, thickness of 0.4mm) with a smooth front face was sprayed, and it was made to deposit. The diameter of the obtained silicon oxide particle was about 3 micrometers. After etching this substrate in a mixed acid, the silicon oxide particle which remained was removed by fluoric acid. The reflection factor in the wavelength of 628nm of the obtained polycrystal silicon substrate was 17%.

[0050] 20g of glass particles with a particle size of about 9 micrometers was added to the solution which carried out equivalent mixing of example 2. isopropyl alcohol and every 500ml of the ethyl acetate, 3ml of aqueous ammonia was added and agitated, and suspension dispersion liquid were prepared. The same polycrystal silicon substrate and same counter electrode as an example 1 were opened and immersed in these dispersion liquid in spacing of several cm, and the direct current voltage of 50-100V was impressed for several minutes. After pulling up a silicon substrate gradually, it heated at 100 degrees C for several minutes. This was etched in the sodium-hydroxide water solution. The reflection factor with a wavelength of 628nm was about 20%.

[0051] The resin solution made to dissolve the resist resin of an example 3. synthetic-rubber system in a xylene was prepared, and the resin solution was screen-stenciled to the same polycrystal silicon substrate as an example 1 through stainless steel line breadth [of about 20 micrometers], and opening size about 30micrometer, and the screen mesh of 25 micrometers of *****. And the substrate was heat-treated for several minutes at 100 degrees C. When the substrate was observed under the microscope, the magnitude of adhering resin was about 30 micrometers. Dry etching of this substrate was carried out by chlorine gas using the parallel monotonous mold RIE system of 13.56MHz high frequency. Processing conditions set gas pressure about 30 mTorr(s), consistency about 0.5 W/cm² of high frequency, and the depth of etching to about 3 micrometers. Next, resin was removed with the oxygen plasma using oxygen gas. The reflection factor with a wavelength of 628nm was 23%.

[0052] The resin solution made to dissolve the resist resin of an example 4. synthetic-rubber system in a xylene was prepared, and it carried out by the same approach as an example 3 except having sprayed the resin solution on one side of the same polycrystal silicon substrate (100mm angle, thickness of 0.4mm) as an example 1 by the spray. The reflection factor with a wavelength of 628nm was about 20%. In addition, when the substrate to which resin was made to adhere was observed under the microscope, the magnitude of adhering resin was 1 micrometer - 30 micrometers in circle configuration.

[0053] The suspension which carried out stirring distribution of the reagent silicon oxide particle of marketing with an example 5. mean particle diameter of 4 micrometers into about 1 wt% water glass (Na₂O-xSiO₂andnH₂O (x=2-4)) was prepared. After putting the barium acetate 0.05wt% solution into the container into which the same polycrystal silicon substrate as an example 1 was put and putting in said suspension subsequently, it put for about 30 minutes, and the

silicon oxide particle was made to deposit on a substrate. The supernatant was removed, the substrate was taken out and it dried after washing with water. After carrying out dry etching of the substrate to which the silicon oxide particle was made to adhere by the same approach as an example 3, the silicon oxide particle which remained was removed by fluoric acid. The reflection factor with a wavelength of 628nm was about 24%.

[0054] The stainless steel mesh which has about 30-micrometer opening in the pitch of about 60 micrometers on the one side was stuck using the same polycrystal silicon substrate as the example 6. example 1, and the RIE system of an example 3 performed dry etching using fluorine system gas. When the cross section of this substrate was observed under the microscope, the crevice of about 30-micrometer width of face was formed in a depth of about 5 micrometers, and the pitch of 60 micrometers. And the reflection factor with a wavelength of 628nm was 24%.

[0055] The polycrystal silicon substrate was rough-cut by the example 7. wire saw. The surface roughness of this substrate was about 5 micrometers, and the reflection factor was 22%. Dry etching of both sides of this substrate was carried out in the plasma of C2F6 gas for about 2 hours using the RIE system of an example 3. The etched thickness was about 10-20 micrometers, and slight surface roughness decreased and was set to about 4 micrometers. The reflection factor with a wavelength [after dry etching] of 628nm was 23%. As a result of forming a solar battery using the substrate after rough cutting, and the substrate after dry etching, conversion efficiency was 7.5% and 12.6%, respectively. Compared with a small difference, the thing with the large difference of conversion efficiency is considered because a mechanical processing damage is on the substrate front face after rough cutting by the reflection factor.

[0056] Two polycrystal silicon substrates which applied resist resin by the spray by the approach of the example 8. example 4 were etched by the same approach as an example 3. One side was etched between two sheets, with the substrate fixed, another side sprayed helium intermittently from the substrate tooth back, and it rocked and it etched it so that it might incline an abundance grade to an electrode stage. The reflection factor with a wavelength of 628nm was 19%, when it fixed and rocked on the other hand 20%.

[0057] It etched in the sodium-hydroxide water solution using the same polycrystal silicon substrate as the example of comparison . example 1. The reflection factor with a wavelength of 628nm was 28%.

[0058]

[Effect of the Invention] As mentioned above, the process which makes the particle for masks distribute and adhere to the front face of a polycrystal silicon substrate on the whole surface according to invention according to claim 1, The process which etches the field where the particle for masks on the front face of a substrate has not adhered, It is the surface roughening approach including the process which removes the particle for masks which remains from the above-mentioned substrate front face, and detailed irregularity is endowed with a substrate front face, and the surface roughening approach of the silicon substrate for solar batteries that the manufacture which raises the photoelectric transfer characteristic of a solar battery is easy, and cheap can be offered.

[0059] Moreover, since according to invention according to claim 2 the particle for masks which consists of silicon oxide with few impurities can be prepared in a short time and adhesion with a substrate can be raised, it has detailed irregularity and a substrate with few impurities can be produced easily.

[0060] Moreover, according to invention according to claim 3, homogeneity can be made to be able to distribute the particle for masks on a substrate according to electrodeposition in a short time, it can be made to adhere, and the substrate which has detailed irregularity can be produced easily.

[0061] Moreover, according to invention according to claim 4, by screen-stenciling the particle for masks on a substrate front face, predetermined spacing can be made dotted with a substrate front face, the particle for masks can be made to adhere, and the substrate which has detailed irregularity can be produced easily.

[0062] Moreover, according to invention according to claim 5, by spraying the particle for masks on a substrate in the state of a minute drop, it can be made to adhere to a substrate, where the particle for masks is distributed, and the substrate which has detailed irregularity can be produced easily.

[0063] Moreover, according to invention according to claim 6, by immersing a substrate in the solution containing the particle for masks, it can be made to adhere to a substrate, where the particle for masks is distributed, and the substrate which has detailed irregularity can be produced easily.

[0064] Moreover, according to invention according to claim 7, it faces making the substrate to which the particle for

masks was made to adhere etch, and the reflection factor of a substrate can be reduced more by making a substrate rock and carrying out dry etching.

[0065] Moreover, according to invention according to claim 8, the particle for masks is made to distribute and adhere to the whole surface, it has the front face of the shape of detailed toothing which removed the particle for masks and was formed after dry etching, and the polycrystal silicon substrate for solar batteries whose reflection factor in the wavelength of 628nm is 25% or less can be offered.

[0066] Moreover, by according to invention according to claim 9, sticking and arranging the screen for masks which has two or more detailed openings on a polycrystal silicon substrate on the whole surface, and carrying out dry etching through the screen, detailed irregularity is endowed with a substrate front face, and the surface roughening approach of the silicon substrate for solar batteries that the manufacture which raises the photoelectric transfer characteristic of a solar battery is easy, and cheap can be offered.

[0067] Moreover, according to invention according to claim 10, in invention of claim 9, the reflection factor of a substrate can be reduced more by making a substrate rock and carrying out dry etching.

[0068] Moreover, according to invention according to claim 11, the screen for masks which has two or more detailed openings is stuck to the whole surface, and is arranged, it has the front face of the shape of detailed toothing formed by carrying out dry etching through the screen, and the reflection factor in the wavelength of 628nm can offer 25% or less of polycrystal silicon substrate for solar batteries.

[0069] Moreover, according to invention according to claim 12, machining cuts a polycrystal silicon substrate rough, by carrying out dry etching, detailed irregularity is endowed with a substrate front face, and the surface roughening approach of the silicon substrate for solar batteries that the manufacture which raises the photoelectric transfer characteristic of a solar battery is easy, and cheap can be offered.

[0070] Moreover, according to invention according to claim 13, it has the front face of the shape of detailed toothing formed by machining cutting a polycrystal silicon substrate rough and carrying out dry etching, and the reflection factor in the wavelength of 628nm can offer 25% or less of polycrystal silicon substrate for solar batteries.

[Translation done.]